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<b>(21) International Application Number:</b> PCT/US96/19353 <b>(22) International Filing Date:</b> 6 December 1996 (06.12.96)  <b>(30) Priority Data:</b> 08/573,176 15 December 1995 (15.12.95) US 08/683,486 18 July 1996 (18.07.96) US 08/757,992 27 November 1996 (27.11.96) US  <b>(71) Applicant:</b> PPG INDUSTRIES, INC. {US/US}; One PPG Place, Pittsburgh, PA 15272 (US).  <b>(72) Inventors:</b> YOLDAS, Bulent, E.; 1605 Jamestown Place, Pittsburgh, PA 15235 (US). PEKALA, Richard, W.; 2102 Henrich Lane, Allison Park, PA 15101 (US). HILL, Charles, T., Jr.; 211 Lynn Drive, New Brighton, PA 15066 (US). ALDERFER, George, E.; 3313 Carriage Drive, Export, PA 15632 (US).  <b>(74) Agents:</b> MORRIS, George, D.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.		<b>(81) Designated States:</b> AU, CA, CH, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> INK-JET PRINTING MEDIA  <b>(57) Abstract</b>  A printing medium which may be ink jet printed to provide images of improved quality comprises a substrate having at least one surface, and a substantially nonporous coating on the surface wherein the coating comprises transparent, colorless alumina monohydroxide and water-soluble organic polymer, and wherein the water-soluble organic polymer comprises water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer. A printing medium which may be ink jet printed eliminates or reduces coalescence of a wide variety of ink jet printing inks and often provides fast drying times. This embodiment comprises: (a) a substrate having at least one surface; and (b) a coating on the surface wherein the coating comprises: (1) a binder comprising organic polymer, wherein poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 20 percent by weight of the organic polymer; and (2) discrete particles dispersed in the binder, which particles have a number average particle size in the range of from 1 to 500 nanometers.		

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## INK-JET PRINTING MEDIA

The present invention is in respect of printing  
5 media which may be ink jet printed and to coating compositions  
which may be used to form the printing media. The invention  
comprises several principal embodiments, or Parts, and various  
embodiments within each Part. Except as noted below, the  
descriptions of the various Parts are substantially  
10 autonomous.

Other than in the operating examples or where  
otherwise indicated, all numbers expressing quantities of  
ingredients or reaction conditions used herein are to be  
understood as modified in all instances by the term "about".  
15

PART I

Ink-jet printing produces little noise and can be  
used to print single color images or multicolor images on  
various substrates. Plain paper or paper having a low degree  
20 of sizing can be used as the printing substrate, but these  
suffer from the disadvantage that a clear image cannot be  
obtained because of the diffusion of the ink into the paper.  
More particularly, the image lacks sharp resolution, and in  
the case of color printing, the image lacks good optical  
25 density.

In order to achieve ink-jet printed images of  
improved quality, coated papers have been employed as the  
printing substrates. The image quality varies depending upon  
the type of coating employed. In most instances image quality  
30 is better than that obtained using uncoated paper, but it is  
still less than desired.

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Similarly, ink-jet printing has been used to print single color images or multicolor images on organic polymer media, but spreading of the ink on organic polymer surfaces presents many problems, including lack of sharp image resolution, and in the case of color printing, the image lacks good optical density. Coatings have provided some improvement, but image quality is still far less than desired.

Ink jet printing inks contain large amounts of solvents. In order to form high quality images, it is necessary for the printing media to quickly remove most of the solvent from the surface of the printing medium and yet retain the colorants within localized areas. One coating used in the past is a porous coating comprising substantially transparent, colorless alumina monohydroxide, e.g., pseudo-boehmite, and organic polymer. Such coatings were porous because it was believed that coating porosity was necessary to accomplish rapid solvent removal. Images of somewhat improved quality were obtained using these coatings, but image quality was still less than desired.

It has now been found that image quality is considerably improved if the coating is substantially nonporous, rather than porous. This is surprising since the solvents of the inks must still be quickly removed from the surface. It has also been found that image quality is improved if water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer are both present. Accordingly, one embodiment of Part I of the invention is a printing medium comprising: (a) a substrate having at least

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one surface; and (b) a substantially nonporous coating on the surface wherein the coating comprises transparent, colorless alumina monohydroxide and water-soluble organic polymer, and wherein the water-soluble organic polymer comprises

5 water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer.

As used herein and in the claims, a coating is substantially nonporous when the pore volume of the coating is less than 0.01 cubic centimeters per gram ( $\text{cm}^3/\text{g}$ ). Often the

10 pore volume of the coating is less than  $0.005 \text{ cm}^3/\text{g}$ . Preferably the pore volume is less than  $0.001 \text{ cm}^3/\text{g}$ . Also as used herein and in the claims, the pore volume of the coating is determined using a Micromeritics Model ASAP 2400 Accelerated Surface Area and Porosimetry Instrument

15 (Micromeritics Instrument Corporation) and nitrogen as the adsorbate in accordance with the accompanying operating manual in which the following choices and modifications are followed:

(a) samples are prepared by drying for 6 hours under vacuum at ambient room temperature, (b) a dried sample weight of

20 approximately 0.2 gram is used, (c) 40 adsorption points are used, (d) 40 desorption points are used, and (e) the BJH cumulative desorption pore volume of the pores having diameters between 1.7 nanometers and 300 nanometers reported by the instrument is taken as the pore volume.

25 Transparent, colorless alumina monohydroxide,  $\text{AlO}(\text{OH})$ , is known. Its preparation and properties are described by B. E. Yoldas in The American Ceramic Society Bulletin, Vol. 54, No. 3, (March 1975), pages 289-290, in Journal of Applied Chemical Biotechnology, Vol. 23 (1973),

30 pages 803-809, and in Journal of Materials Science, Vol. 10 (1975), pages 1856-1860. Briefly, aluminum isopropoxide or aluminum secondary-butoxide are hydrolyzed in an excess of

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water with vigorous agitation at from 75 C to 80°C to form a slurry of aluminum monohydroxide. The aluminum monohydroxide is then peptized at temperatures of at least 80°C with an acid to form a clear alumina monohydroxide sol which exhibits the Tyndall effect when illuminated with a narrow beam of light. Since the alumina monohydroxide of the sol is neither white nor colored, it is not a pigment and does not function as a pigment in the present invention. The acid employed is noncomplexing with aluminum, and it has sufficient strength to produce the required charge effect at low concentration. Nitric acid, hydrochloric acid, perchloric acid, acetic acid, chloroacetic acid, and formic acid meet these requirements. The acid concentration is usually in the range of from 0.03 to 0.1 mole of acid per mole of aluminum alkoxide. Although it is desired not to be bound by any theory, it is believed that the alumina monohydroxide produced in this manner is pseudo-boehmite. Pseudo-boehmite is indeed the preferred transparent, colorless alumina monohydroxide for use in the present invention.

The amount of transparent, colorless alumina monohydroxide in the coating may vary widely. Often the transparent, colorless alumina monohydroxide constitutes from 10 to 87 percent by weight of the coating. In many cases the transparent, colorless alumina monohydroxide constitutes from 50 to 85 percent by weight of the coating. From 70 to 85 percent by weight is preferred.

The water-soluble organic polymer comprises water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer. Organic polymer of either or both classes may or may not be insolubilized as desired. As used herein and in the claims, insolubilized water-soluble organic polymer is organic polymer which is water-soluble when

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applied to the substrate and which is completely or partially insolubilized after such application. Preferably the insolubilizer reacts with water-soluble noncellulosic organic polymer to provide the desired degree of insolubilization to the total organic polymer of the coating.

There are many widely varying types of water-soluble cellulosic organic polymers which may be employed in the present invention. Of these, the water-soluble cellulose ethers are preferred water-soluble cellulosic organic polymers. Many of the water-soluble cellulose ethers are also excellent water retention agents. Examples of the water-soluble cellulose ethers include water-soluble methylcellulose [CAS 9004-67-5], water-soluble carboxymethylcellulose, water-soluble sodium carboxymethylcellulose [CAS 9004-32-4], water-soluble ethylmethylcellulose, water-soluble hydroxyethylmethylcellulose [CAS 9032-42-2], water-soluble hydroxypropylmethylcellulose [CAS 9004-65-3], water-soluble hydroxyethylcellulose [CAS 9004-62-0], water-soluble ethylhydroxyethylcellulose, water-soluble sodium carboxymethylhydroxyethylcellulose, water-soluble hydroxypropylcellulose [CAS 9004-64-2], water-soluble hydroxybutylcellulose [CAS 37208-08-5], water-soluble hydroxybutylmethylcellulose [CAS 9041-56-9] and water-soluble cellulose sulfate sodium salt [CAS 9005-22-5]. Water-soluble hydroxypropylcellulose is preferred.

Water-soluble hydroxypropylcellulose is a known material and is available commercially in several different average molecular weights. The weight average molecular weight of the water-soluble hydroxypropylcellulose used in the present invention can vary widely, but usually it is in the range of from 100,000 to 1,000,000. Often the weight average

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molecular weight is in the range of from 100,000 to 500,000. From 200,000 to 400,000 is preferred. Two or more water-soluble hydroxypropylcelluloses having different average molecular weights may be admixed to obtain a water-soluble  
5 hydroxypropyl cellulose having a differing average molecular weight.

Similarly, there are many widely varying kinds of water-soluble noncellulosic organic polymers which may be employed in the present invention. Examples of the  
10 water-soluble noncellulosic organic polymers include water-soluble poly(vinyl alcohol), water-soluble poly(vinylpyrrolidone), water-soluble poly(vinylpyridine), water-soluble poly(ethylene oxide), water-soluble poly(ethylenimine), water-soluble ethoxylated  
15 poly(ethylenimine), water-soluble poly(ethylenimine)-epichlorohydrin, water-soluble polyacrylate, water-soluble sodium polyacrylate, water-soluble poly(acrylamide), water-soluble carboxy modified poly(vinyl alcohol), water-soluble poly(2-acrylamido-2-methylpropane sulfonic  
20 acid), water-soluble poly(styrene sulfonate), water-soluble vinylmethyl ether/maleic acid copolymer, water-soluble styrene-maleic anhydride copolymer, water-soluble ethylene-maleic anhydride copolymer, water-soluble acrylamide/acrylic acid copolymer, water-soluble poly(diethylene triamine-co-  
25 adipic acid), water-soluble poly[(dimethylamino)ethyl methacrylate hydrochloride], water-soluble quaternized poly(imidazoline), water-soluble poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride),  
poly(dimethyldiallylammonium chloride),  
30 poly(vinylbenzyltrimethylammonium chloride), water-soluble poly(vinylpyridinium halide), water-soluble poly[(methacryloyloxyethyl)(2-hydroxyethyl)dimethylammonium



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chloride], water-soluble poly(alkylenepolyaminedicyandiamide ammonium condensate), water-soluble poly((meth)acrylamidealkyl quaternary salts, water-soluble starch, water-soluble oxidized starch, water-soluble cationized starch, water-soluble casein, 5 water-soluble gelatin, water-soluble sodium alginate, water-soluble carrageenan, water-soluble dextran, water-soluble gum arabic, water-soluble pectin, water-soluble albumin, and water-soluble agar-agar. Water-soluble poly(vinyl alcohol) is preferred.

10 Water-soluble poly(vinyl alcohol) may be broadly classified as one of two types. The first type is fully hydrolyzed water-soluble poly(vinyl alcohol) in which less than 1.5 mole percent acetate groups are left on the molecule.

The second type is partially hydrolyzed water-soluble 15 poly(vinyl alcohol) in which from 1.5 to as much as 20 mole percent acetate groups are left on the molecule. The water-soluble organic polymer may comprise either type or a mixture of both. The fully hydrolyzed water-soluble poly(vinyl alcohol) is preferred.

20 The amount of water-soluble organic polymer in the coating may vary widely. Often the water-soluble organic polymer constitutes from 13 to 90 percent by weight of the coating. In many cases the water-soluble organic polymer constitutes from 15 to 50 percent by weight of the coating. 25 From 15 to 30 percent by weight is preferred.

The water-soluble organic polymer of the coating comprises water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer. Usually the water-soluble cellulosic organic polymer constitutes from 5 to 30 95 percent by weight of the water-soluble organic polymer and the water-soluble noncellulosic organic polymer constitutes from 5 to 95 percent by weight of the water-soluble organic

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polymer. Frequently the water-soluble cellulosic organic polymer constitutes from 30 to 90 percent by weight of the water-soluble organic polymer and the water-soluble noncellulosic organic polymer constitutes from 10 to 70 percent by weight of the water-soluble organic polymer. Preferably the water-soluble cellulosic organic polymer constitutes from 60 to 80 percent by weight of the water-soluble organic polymer and the water-soluble noncellulosic organic polymer constitutes from 20 to 40 percent by weight of the water-soluble organic polymer.

The coating comprising transparent, colorless alumina monohydroxide and organic polymer may itself be substantially transparent, substantially opaque, or of intermediate transparency. It may be substantially colorless, it may be highly colored, or it may be of an intermediate degree of color. Preferably the coating comprising transparent alumina monohydroxide and organic polymer is itself substantially transparent and substantially colorless.

As used herein and in the claims, the coating is substantially transparent if the luminous transmission in the visible region is at least 80 percent of the incident light. Often the luminous transmission is at least 85 percent of the incident light. Preferably the luminous transmission is at least 90 percent. Also as used herein and in the claims, the coating is substantially colorless if the transmission is substantially the same for all wavelengths in the visible region.

The substrate may be any substrate at least one surface of which is capable of bearing the coating discussed above. In most instances the substrate is in the form of an individual sheet or in the form of a roll, web, strip, film, or foil of material capable of being cut into sheets.

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The substrate may be porous throughout, but it is preferred that printing medium comprise: (a) a substrate having at least one substantially nonporous surface; and (b) a substantially nonporous coating on the surface wherein the coating comprises transparent, colorless alumina monohydroxide and organic polymer, and wherein the water-soluble organic polymer comprises water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer.

An example of a porous substrate is paper. Another example is cloth.

When, as is preferred, the substrate has at least one substantially nonporous surface, the substrate may be substantially nonporous throughout or the surface may be substantially nonporous irrespective of how much of the remainder of the substrate is porous.

Examples of substrates which are substantially nonporous throughout and hence have at least one substantially nonporous surface, include sheets or films of organic polymer such as poly(ethylene terephthalate), polyethylene, polypropylene, cellulose acetate, and copolymers such as saran. Additional examples include metal foils such as aluminum foil. Yet another example is a porous or microporous foam comprising thermoplastic organic polymer which foam has been compressed to such an extent that the resulting deformed material is substantially nonporous.

The substrate may or may not include one or more coatings or laminations between the base stock and the substantially nonporous coating which comprises alumina monohydroxide and organic polymer and which is described above.

Base stocks which are normally porous such as for example paper, cloth, nonwoven fabric, felt, porous foam, or

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microporous foam may be coated or laminated to render one or more surfaces substantially nonporous and thereby provide substrates having at least one substantially nonporous surface.

5           The substrate may be substantially transparent, it may be substantially opaque, or it may be of intermediate transparency. For some applications such as ink-jet printed overhead slides, the substrate must be sufficiently transparent to be useful for the application. For other  
10 applications such as ink-jet printed paper, transparency of the substrate is not so important.

          The printing media of Part I of the invention may be made by coating a substantially nonporous surface of the substrate with a coating composition comprising: (a)  
15 transparent, colorless alumina monohydroxide; (b) aqueous solvent; and (c) water-soluble organic polymer dissolved in the aqueous solvent; wherein the water-soluble organic polymer comprises water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer.

20           The discussions above in respect of the alumina monohydroxide, the water-soluble cellulosic organic polymer, and the water-soluble noncellulosic organic polymer, are applicable here.

          The weight ratio of the alumina monohydroxide to  
25 water-soluble organic polymer in the coating composition may vary considerably, but it is usually in the range of from 11:100 to 670:100. Often the weight ratio is in the range of from 100:100 to 567:100. Preferably it is in the range of from 233:100 to 567:100.

30           The discussions above in respect of the proportions of water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer water-soluble organic polymer in

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the water-soluble organic polymer, are applicable to the coating composition as well as to the coating.

In most instances the aqueous solvent is water. Organic cosolvents miscible with water may optionally be present when desired. The amount of aqueous solvent present in the coating composition may vary widely. The minimum amount is that which will produce a coating composition having a viscosity low enough to apply as a coating. The maximum amount is not governed by any theory, but by practical considerations such as the cost of the solvent, the minimum desired thickness of the coating to be deposited, and the cost and time required to remove the solvent from the applied wet coating. Usually, however, the aqueous solvent constitutes from 80 to 98 percent by weight of the coating composition. Often the aqueous solvent constitutes from 85 to 95 percent by weight of the coating composition. Preferably aqueous solvent constitutes from 85 to 90 percent by weight of the composition.

A material which may optionally be present in the coating composition is insolubilizer. Insolubilizers are materials which react with functional groups of water-soluble organic polymers, especially those of water-soluble noncellulosic organic polymers, and generally function as crosslinking agents. There are many available insolubilizers which may be used. Examples of suitable insolubilizers include, but are not limited to, Curesan® 199 insolubilizer (PPG Industries, Inc., Pittsburgh, PA), Curesan® 200 insolubilizer (PPG Industries, Inc.), Sequarez® 700C insolubilizer (Sequa Chemicals, Inc., Chester, SC), Sequarez® 700M insolubilizer (Sequa Chemicals, Inc.), Sequarez® 755 insolubilizer (Sequa Chemicals, Inc.), Sequarez® 770 insolubilizer (Sequa Chemicals, Inc.),

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Berset® 39 insolubilizer (Bercen Inc., Cranston, RI),  
Berset® 47 insolubilizer (Bercen Inc.), Berset® 2185  
insolubilizer (Bercen Inc.), and Berset® 2586 insolubilizer  
(Bercen Inc.).

5           When used, the amount of insolubilizer present in  
the coating composition may vary considerably. In such  
instances the weight ratio of the insolubilizer to the  
water-soluble noncellulosic organic polymer is usually in the  
range of from 0.05:100 to 25:100. Often the weight ratio is  
10 in the range of from 2:100 to 10:100. From 4:100 to 6:100 is  
preferred. These ratios are on the basis of insolubilizer dry  
solids and water-soluble noncellulosic organic polymer dry  
solids.

          There are many other materials which may optionally  
15 be present in the coating composition. These include such  
materials as lubricants, waxes, antioxidants, organic  
solvents, mordants, lakes, and pigments. The listing of such  
materials is by no means exhaustive. These and other  
ingredients may be employed in their customary amounts for  
20 their customary purposes so long as they do not seriously  
interfere with good coating composition formulating practice.

          The coating compositions are usually prepared by  
simply admixing the various ingredients. The ingredients may  
be mixed in any order, but it is preferred to mix the dry  
25 ingredients together before mixing with liquid. Although the  
mixing of liquid and solids is usually accomplished at room  
temperature, elevated temperatures are sometimes used. The  
maximum temperature which is usable depends upon the heat  
stability of the ingredients.

30           The coating compositions are generally applied to  
the surface of the substrate using substantially any technique  
known to the art. These include spraying, curtain coating,

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dipping, rod coating, blade coating, roller application, size press, printing, brushing, drawing, die-slot coating, and extrusion. The coating is then formed by removing the solvent from the applied coating composition. This may be  
5 accomplished by any conventional drying technique. Coating composition may be applied once or a multiplicity of times. When the coating composition is applied a multiplicity of times, the applied coating is usually but not necessarily dried, either partially or totally, between coating  
10 applications. Once the coating composition has been applied to the paper, the solvent is substantially removed, usually by drying.

Optionally the substantially nonporous coating containing the transparent alumina monohydroxide and  
15 water-soluble organic polymer may be overlaid with an overcoating comprising ink-receptive organic polymer. The overcoating may be formed by applying an overcoating composition comprising solvent and ink-receptive organic polymer dissolved in the solvent and removing the solvent, as  
20 for example, by drying. Preferably the solvent is an aqueous solvent and the ink-receptive organic polymer is water-soluble cellulosic organic polymer, both of which have been described above in respect of the alumina monohydroxide-containing coating. Water is an especially preferred aqueous solvent and  
25 hydroxypropylcellulose is an especially preferred water-soluble cellulosic organic polymer.

The relative proportions of aqueous solvent and organic polymer present in the overcoating composition may vary widely. The minimum proportion is that which will  
30 produce an overcoating composition having a viscosity low enough to apply as an overcoating. The maximum proportion is not governed by any theory, but by practical considerations

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such as the cost of the solvent and the cost and time required to remove the solvent from the applied wet overcoating.

Usually, however, the weight ratio of aqueous solvent to organic polymer is from 18:1 to 50:1. Often the weight ratio is from 19:1 to 40:1. Preferably weight ratio is from 19:1 to 24:1.

Optional ingredients such as those discussed above may be present when desired.

The overcoating composition may be prepared by admixing the ingredients. It may be applied and dried using any of the coating and drying techniques discussed above. When an overcoating composition is to be applied, it may be applied once or a multiplicity of times.

After the coating has been substantially dried, the coated substrate may optionally be calendered. In most cases calendering is accomplished between two rolls. Preferably, but not necessarily, the roll contacting the coating of the coated substrate is a metal-surfaced roll. The other roll is preferably, but not necessarily, surfaced with a somewhat resilient material such as an elastomer of medium hardness. When calendering is employed, the roll temperature may be widely varied, but usually the roll temperature is in the range of from 20°C to 100°C. Often the roll temperature is in the range of from 30°C to 80°C. From 40°C to 60°C is preferred. Similarly, the force per unit length of the nip may be widely varied. Frequently the force per unit length of the nip is in the range of from 85 to 350 kilonewtons per meter (kN/m). In many instances the force per unit length of the nip is in the range of from 120 to 275 kN/m. Preferably it is in the range of from 155 to 200 kN/m.

The gloss of the coated substrate may vary widely. Although lower glosses are acceptable for many purposes, it is



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preferred that the gloss be at least 20. As used herein gloss is determined according to TAPPI Standard T480 om-92.

Part I of the invention is further described in conjunction with the following examples which are to be  
5 considered illustrative rather than limiting, and in which all parts are parts by weight and all percentages are percentages by weight unless otherwise specified.

#### EXAMPLE 1

10 With stirring, 248 grams of aluminum tri-sec-butoxide [CAS 2269-22-9] was added to 2 liters of water at 70°C in a glass container. To this mixture 6 grams of 60 percent concentrated nitric acid was added. The reaction mixture was stirred for 15 minutes on a hot plate. The glass  
15 container containing the reaction mixture was then sealed with a lid and placed in an oven at 95°C for 2 days. During the two-day period in the oven the precipitate in the reaction mixture was peptized. The resulting colloidal dispersion was concentrated in an unsealed container to 600 grams by boiling  
20 to produce a colloidal dispersion (sol) containing 10 percent by weight colloidal alumina monohydroxide.

#### EXAMPLE 2

To 300 grams of alumina monohydroxide sol prepared  
25 as in Example 1 was added 6 grams of hydroxypropyl cellulose (HPC) having a weight average molecular weight of 370,000 (Aldrich Chemical Company, Inc.), and 3 grams of Airvol® 205S poly(vinyl alcohol) (Air Products and Chemicals Inc.). The mixture was stirred until the HPC and the poly(vinyl alcohol)  
30 (PVA) had completely dissolved giving a coating composition containing about 13 percent solids. The coating composition was applied to poly(ethylene terephthalate) (PET)

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transparencies with a Meyer Rod ( $13.7 \text{ g/m}^2$ ) and allowed to dry at room temperature. The coating was about  $20 \text{ }\mu\text{m}$  thick and clear. The coated transparencies were then printed by an HP-350 ink jet printer. The ink jet printed transparencies exhibited excellent ability to maintain the edge acuity of ink patterns, excellent color fidelity, and resistance against scratches.

#### EXAMPLE 3

Example 2 was repeated except that one gram of 3-methacryloxypropyltrimethoxysilane [CAS 2530-85-0] was added to each 100 grams of coating composition prepared as in Example 2. The dry coating and ink jet printed transparencies showed excellent water resistance after being soaked in water for one hour.

#### EXAMPLE 4

One gram of tetramethyl orthosilicate [CAS 681-84-5] was added to each 100 grams of coating composition prepared as in Example 2. After several hours the resulting coating composition was applied to PET transparencies in a manner similar to that of Example 2. After the coating had dried, the coated transparencies were ink jet printed. The ink jet printed transparencies exhibited water fastness when soaked in water for a period of hours.

#### EXAMPLE 5

To 100 grams of alumina monohydroxide sol prepared as in Example 1 was added 5 grams of HPC having a weight average molecular weight of 370,000, 2 grams of Airvol® 205S PVA, and 70 grams of water. The mixture was stirred until the HPC and PVA had dissolved. The resulting coating composition

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was applied to PET transparencies in a manner similar to that of Example 2. After the coating had dried, the coated transparencies were ink jet printed on an Epson ink jet printer. The quality of the ink jet printed transparencies was excellent.

#### EXAMPLE 6

To 100 grams of alumina monohydroxide sol prepared as in Example 1 was added 2 grams of HPC having a weight average molecular weight of 370,000, 2 grams of Airvol® 205S PVA, 2 grams of poly(vinyl pyrrolidone) [CAS 9003-39-8] (Aldrich Chemical Company, Inc.) (PVP) having a weight average molecular weight of 10,000, and 50 grams of water. The mixture was stirred until the HPC, PVA, and PVP had dissolved.

The resulting coating composition was applied to PET transparencies in a manner similar to that of Example 2. After the coating had dried, the coated transparencies were ink jet printed on an Epson ink jet printer. Not only was the quality of the ink jet printed transparencies excellent, but the inks dried much faster than on many commercially available transparencies.

#### EXAMPLE 7

To 100 grams of alumina monohydroxide sol prepared as in Example 1 was added 3.5 grams of Airvol® 205S PVA, 1.5 grams of PVP having a weight average molecular weight of 10,000, and one gram of 3-methacryloxypropyltrimethoxysilane. The mixture was stirred until the PVA and PVP had dissolved and then allowed to stand overnight. The resulting coating composition was applied to PET transparencies in a manner similar to that of Example 2. After the coating had dried, the coated transparencies were ink jet printed by an HP-855

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ink jet printer which is a heaterless printer. The ink dried within 30-60 seconds and the ink jet printed transparencies were of excellent quality.

5

EXAMPLE 8

To 150 grams of alumina monohydroxide sol prepared as in Example 1 was added one gram of HPC having a weight average molecular weight of 370,000, 2 grams of Airvol® 205S PVA, one gram of PVP having a weight average molecular weight  
10 of 10,000, and 1.5 grams of 3-methacryloxypropyltrimethoxysilane mixed in 10 grams of ethanol. The mixture was stirred until the HPC, PVA, and PVP had dissolved. The resulting coating composition was applied to PET transparencies in a manner similar to that of  
15 Example 2. After the coating had dried, the coated transparencies were ink jet printed by an HP-855 ink jet printer. The ink dried quickly and the ink jet printed transparencies were water resistant and of excellent quality.

20

EXAMPLE 9

A solution was prepared by dissolving 10 grams of HPC having a weight average molecular weight of 370,000 and 5 grams of Airvol® 205S PVA in 285 grams of water. Portions of this solution were admixed with portions of alumina  
25 monohydroxide sol prepared as in Example 1 to form a series of coating compositions having varying organic polymer to alumina monohydroxide ratios. These coating compositions were applied to glass substrates and to PET transparencies. The wet coatings were then dried at room temperature. The dried  
30 coatings were peeled from the glass substrates with a blade and the pore volumes were ascertained using the procedure earlier described. The weight percents of organic polymer in

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the dry coatings and the corresponding pore volumes are shown in Table 1.

TABLE 1

5

<u>Sample No.</u>	<u>Organic Polymer, weight percent</u>	<u>Pore Volume, (cm<sup>3</sup>/g)</u>
1	0	0.2240
2	3	0.2008
3	7	0.1519
4	11	0.0797
5	13	0.0096
6	14	0.0008
7	18	0.0007

The data show that when the organic polymer constitutes 13 weight percent or more of the dry coating, the coating is substantially nonporous with a common standard of  
10 discernment. Similar coating compositions containing no alumina monohydroxide provide dry coatings having pore volumes of from 0.0005 to 0.0010 cm<sup>3</sup>/g.

EXAMPLE 10

15

To 300 grams of alumina monohydroxide sol prepared as in Example 1 was added 9 grams of HPC having a weight average molecular weight of 370,000, 6 grams of Airvol® 205S PVA. The mixture was stirred until the HPC and PVA had dissolved. The product was a first coating composition.

20

Nine grams of HPC having a molecular weight of 370,000, nine grams of Airvol® 205S PVA, and 16.7 grams of 45 weight percent solids Luviskol® K 60 poly(vinyl pyrrolidone) (BASF Corp.) were dissolved in 220 grams of water to form a second coating composition.

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The first coating composition was applied to photographic resin coated basestock at a coating weight of 11.8 g/m<sup>2</sup> using a hand drawn Meyer Rod applicator and air dried at room temperature to form a first coating. The second coating composition was applied to the first coating at a coating weight of 11.8 g/m<sup>2</sup> using a hand drawn Meyer Rod applicator and air dried at room temperature to form a second coating. The resulting articles were high gloss printing sheets.

The above high gloss sheets were printed on an Epson Color Stylist Ink Jet Printer and a Canon BJC 610 Ink Jet Printer. The print densities are shown in Table 2.

TABLE 2

<u>Printer</u>	<u>Black</u>	<u>Cyan</u>	<u>Magenta</u>	<u>Yellow</u>
Epson	2.38	1.97	1.67	0.87
Canon	2.40	1.86	1.55	1.08

The data show that the print densities were exceptionally good. Edge acuity, wicking, and bleed were estimated visually. The results were also exceptionally favorable in each of these categories.

PART II

A considerable problem that has arisen from the use of coatings for ink jet printing media is that many of the inks used for ink jet printing coalesce on many of the coatings. There are, unfortunately, many different kinds of inks which are used for ink jet printing and a coated substrate which performs satisfactorily with inks of one type

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frequently performs less than satisfactorily with inks of another type.

Another problem that has arisen from the use of coated substrates as ink jet printing media is the long drying  
5 time of the water-based inks after they have been applied to the coated substrates.

A coated substrate has now been found which eliminates or reduces coalescence of a wide variety of ink jet printing inks when applied to the coated substrate and which  
10 often provides fast drying times. Accordingly, one embodiment of Part II of the invention is a printing medium comprising:  
(a) a substrate having at least one surface; and (b) a coating on the surface wherein the coating comprises: (1) a binder comprising mainly organic polymer, wherein poly(ethylene  
15 oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 20 percent by weight of the organic polymer; and (2) discrete particles dispersed in the binder, which particles have a number average particle size in the range of from 1 to 500 nanometers. In  
20 this embodiment the coating may be substantially nonporous or it may be porous.

The number average particle size of the particles is in the range of from 1 to 500 nanometers. Often the number average particle size is in the range of from 1 to 100  
25 nanometers. Frequently the number average particle size is in the range of from 1 to 50 nanometers. Preferably the number average particle size is in the range of from 1 to 20 nanometers.

As used herein and in the claims number average  
30 particle size is determined by transmission electron microscopy.

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The amount of the discrete particles in the coating may vary widely. Often the particles constitute from 20 to 70 percent by weight of the coating. In many cases the particles constitute from 40 to 60 percent by weight of the coating.

5 From 45 to 55 percent by weight is preferred.

The discrete particles may be discrete inorganic particles, discrete crosslinked organic particles, or a mixture thereof.

The discrete particles are often discrete particles  
10 of metal oxide. The metal oxide constituting the particles may be a simple metal oxide (i.e., the oxide of a single metal) or it may be a complex metal oxide (i.e., the oxide of two or more metals). The particles of metal oxide may be particles of a single metal oxide or they may be a mixture of  
15 different particles of different metal oxides.

Examples of suitable metal oxides include alumina, silica, and titania. Other oxides may optionally be present in minor amount. Examples of such optional oxides include, but are not limited to, zirconia, hafnia, and yttria. Other  
20 metal oxides that may optionally be present are those which are ordinarily present as impurities such as for example, iron oxide. For purposes of the present specification and claims, silicon is considered to be a metal.

When the particles are particles of alumina, most  
25 often the alumina is alumina monohydroxide. Particles of alumina monohydroxide,  $\text{AlO}(\text{OH})$ , and their preparation are known. The preparation and properties of alumina monohydroxide are described by B. E. Yoldas in The American Ceramic Society Bulletin, Vol. 54, No. 3, (March 1975),  
30 pages 289-290, in Journal of Applied Chemical Biotechnology, Vol. 23 (1973), pages 803-809, and in Journal of Materials Science, Vol. 10 (1975), pages 1856-1860. Briefly, aluminum



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isopropoxide or aluminum secondary-butoxide are hydrolyzed in an excess of water with vigorous agitation at from 75 C to 80°C to form a slurry of aluminum monohydroxide. The aluminum monohydroxide is then peptized at temperatures of at least 5 80°C with an acid to form a clear alumina monohydroxide sol which exhibits the Tyndall effect when illuminated with a narrow beam of light. Since the alumina monohydroxide of the sol is neither white nor colored, it is not a pigment and does not function as a pigment in the present invention. The acid 10 employed is noncomplexing with aluminum, and it has sufficient strength to produce the required charge effect at low concentration. Nitric acid, hydrochloric acid, perchloric acid, acetic acid, chloroacetic acid, and formic acid meet these requirements. The acid concentration is usually in the 15 range of from 0.03 to 0.1 mole of acid per mole of aluminum alkoxide. Although it is desired not to be bound by any theory, it is believed that the alumina monohydroxide produced in this manner is pseudo-boehmite. Pseudo-boehmite is indeed the preferred alumina monohydroxide for use in the present 20 invention. The alumina monohydroxide is not a pigment and does not function as a pigment in the present invention. In most instances the alumina monohydroxide is transparent and colorless.

Colloidal silica is also known. Its preparation and 25 properties are described by R. K. Iler in The Chemistry of Silica, John Wiley & Sons, Inc., New York (1979) ISBN 0-471-02404-X, pages 312-337, and in United States Patents No. 2,601,235; 2,614,993; 2,614,994; 2,617,995; 2,631,134; 2,885,366; and 2,951,044, the disclosures of which 30 are, in their entireties, incorporated herein by reference. Examples of commercially available colloidal silica include Ludox® HS, LS, SM, TM and CL-X colloidal silica (E. I. du Pont

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de Nemours & Company, Inc.) in which the counter ion is the sodium ion, and Ludox® AS colloidal silica (E. I. du Pont de Nemours & Company, Inc.) in which the counter ion is the ammonium ion. Another example is Ludox® AM colloidal silica  
5 (E. I. du Pont de Nemours & Company, Inc.) in which some of the silicon atoms have been replaced by aluminum atoms and the counter ion is the sodium ion.

Colloidal titania is also known. Its preparation and properties are described in United States Patent No.  
10 4,275,118. Colloidal titania may also be prepared by reacting titanium isopropoxide [CAS 546-68-9] with water and tetramethyl ammonium hydroxide.

The discrete particles are frequently discrete particles of crosslinked organic polymer. Examples of such  
15 crosslinked organic polymer include crosslinked melamine-formaldehyde polymer, crosslinked resorcinol-formaldehyde polymer, crosslinked phenol-resorcinol-formaldehyde polymer, crosslinked (meth)acrylate polymer, and crosslinked styrene-divinylbenzene polymer.

20 The binder functions as a matrix for the discrete particles dispersed therein. The binder comprises mainly organic polymer but it may optionally contain minor amounts of conventional adjuvants as will be discussed more fully later in connection with the coating composition used to form the  
25 coating of the printing medium. The binder of the coating comprises film-forming organic polymer or insolubilized film-forming organic polymer. The film-forming polymer may be water-soluble or water-dispersible organic polymer.

Poly(ethylene oxide) having a weight average  
30 molecular weight in the range of from 100,000 to 3,000,000 is known. Such materials are ordinarily formed by polymerizing ethylene oxide [CAS 75-21-8], usually in the presence of a

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small amount of an initiator such as low molecular weight glycol or triol. Examples of such initiators include ethylene glycol [CAS 107-21-1], diethylene glycol [CAS 111-46-6], triethylene glycol [CAS 112-27-6], tetraethylene glycol [CAS 112-60-7], propylene glycol [CAS 57-55-6], trimethylene glycol [CAS 504-63-2], dipropylene glycol [CAS 110-98-5], glycerol [CAS 56-81-5], trimethylolpropane [CAS 77-99-6], and  $\alpha,\omega$ -diaminopoly(propylene glycol) [CAS 9046-10-0]. One or more other lower alkylene oxides such as propylene oxide [CAS 75-56-9] and trimethylene oxide [CAS 503-30-0] may also be employed as comonomer with the ethylene oxide, whether to form random polymers or block polymers, but they should be used only in those small amounts as will not render the resulting polymer both water-insoluble and nondispersible in water. As used herein and in the claims, the term "poly(ethylene oxide)" is intended to include the foregoing copolymers of ethylene oxide with small amounts of lower alkylene oxide, as well as homopolymers of ethylene oxide. The configuration of the poly(ethylene oxide) can be linear, branched, comb, or star-shaped. The preferred terminal groups of the poly(ethylene oxide) are hydroxyl groups, but terminal lower alkoxy groups such as methoxy groups may be present provided their types and numbers do not render the poly(ethylene oxide) polymer unsuitable for its purpose. In most cases the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 is water-insoluble. The preferred poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 is a water-soluble homopolymer of ethylene oxide produced using a small amount of ethylene glycol as an initiator.

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The weight average molecular weight of the poly(ethylene oxide) is in the range of from 100,000 to 3,000,000. Often the weight average molecular weight of the poly(ethylene oxide) is in the range of from 150,000 to 1,000,000. Frequently the weight average molecular weight of the poly(ethylene oxide) is in the range of from 200,000 to 1,000,000. From 300,000 to 700,000 is preferred.

The amount of organic polymer of the binder in the coating may vary widely. Often the organic polymer of the binder constitutes from 30 to 80 percent by weight of the coating. In many cases the organic polymer of the binder constitutes from 40 to 60 percent by weight of the coating. From 45 to 55 percent by weight is preferred.

The organic polymer of the binder may optionally also comprise additional organic polymer other than poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000. Such additional organic polymers are film-forming organic polymers or insolubilized film-forming organic polymers. Examples of additional film-forming organic polymers include, but are not limited to, water-soluble poly(ethylene oxide) having a weight average molecular weight below 100,000, water-soluble poly(ethylene oxide) having a weight average molecular weight above 3,000,000, water-soluble cellulosic organic polymers such as those heretofore described in respect of Part I, water-soluble noncellulosic organic polymers such as those heretofore described in respect of Part I, water dispersible polymers such as poly(ethylene-co-acrylic acid), or a mixture of two or more thereof. Both of such Part I descriptions are, in their entirety, incorporated herein by reference. Examples of water-soluble polyacrylates which can advantageously be used include the water-soluble anionic

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polyacrylates and the water-soluble cationic polyacrylates.  
Water-soluble anionic polyacrylates are themselves well known.

Usually, but not necessarily, they are copolymers of one or more (meth)acrylic esters and enough (meth)acrylic acid and/or  
5 (meth)acrylic acid salt to provide sufficient carboxylate anions to render the polymer water-soluble. Similarly, water-soluble cationic polyacrylates are themselves well known. Usually, but not necessarily, they are copolymers of one or more (meth)acrylic esters and enough amino-functional  
10 ester of (meth)acrylic acid to provide sufficient ammonium cations to render the acrylic polymer water-soluble. Such ammonium cations may be primary, secondary, tertiary, or quaternary. Usually the water soluble cationic polyacrylate is a primary, secondary, tertiary, or quaternary ammonium  
15 salt, or it is a quaternary ammonium hydroxide.

After application of the coating composition to the substrate surface, the film-forming organic polymer may optionally be reacted with crosslinking agent (also known as insolubilizer) to form insolubilized organic polymer.

20 Examples of crosslinking agents and their amounts are disclosed in Part I and such disclosures are, in their entirety, incorporated herein by reference.

Usually the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to  
25 3,000,000 constitutes at least 20 percent by weight of the organic polymer of the binder. Generally the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 51 percent by weight of the organic polymer of the binder. In many  
30 instances the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 60 percent by weight of the organic

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polymer of the binder. Often the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 90 percent by weight of the organic polymer of the binder. Frequently the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 95 percent by weight of the organic polymer of the binder. In many cases the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 99 percent by weight of the organic polymer of the binder. In some cases the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes 100 percent by weight of the organic polymer of the binder.

When optional additional organic polymer is present in the binder, it usually constitutes from 1 to 80 percent by weight of the organic polymer of the binder. Frequently the optional additional organic polymer constitutes from 1 to 49 percent by weight of the organic polymer of the binder. In many cases the optional additional organic polymer constitutes from 1 to 40 percent by weight of the organic polymer of the binder. Often the optional additional organic polymer constitutes from 1 to 10 percent by weight of the organic polymer of the binder. Frequently the optional additional organic polymer constitutes from 1 to 5 percent by weight of the organic polymer of the binder.

The coating may be substantially transparent, substantially opaque, or of intermediate transparency. It may be substantially colorless, it may be highly colored, or it may be of an intermediate degree of color. Preferably the coating is substantially transparent and substantially colorless. As used herein and in the claims, a coating is

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substantially transparent if its luminous transmission in the visible region is at least 80 percent of the incident light. Often the luminous transmission of the coating is at least 85 percent of the incident light. Preferably the luminous  
5 transmission of the coating is at least 90 percent. Also as used herein and in the claims, a coating is substantially colorless if the luminous transmission is substantially the same for all wavelengths in the visible region, viz., 400 to 800 nanometers.

10 The thickness of the coating may vary widely, but in most instances the thickness of the coating is in the range of from 1 to 40  $\mu\text{m}$ . In many cases the thickness of the coating is in the range of from 5 to 40  $\mu\text{m}$ . Often the thickness is in the range of from 8 to 30  $\mu\text{m}$ . From 12 to 18  $\mu\text{m}$  is preferred.

15 The substrate may be any substrate at least one surface of which is capable of bearing the coating discussed above. In most instances the substrate is in the form of an individual sheet or in the form of a roll, web, strip, film, or foil of material capable of being cut into sheets.

20 The substrate may be porous throughout, it may be nonporous throughout, or it may comprise both porous regions and nonporous regions.

Examples of porous substrates include paper, paperboard, wood, cloth, nonwoven fabric, felt, unglazed  
25 ceramic material, polymer membranes, porous foam, and microporous foam.

Examples of substrates which are substantially nonporous throughout include sheets or films of organic polymer such as poly(ethylene terephthalate), polyethylene,  
30 polypropylene, cellulose acetate, poly(vinyl chloride), and copolymers such as saran. The sheets or films may be metallized or unmetallized as desired. Additional examples

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include metal substrates including but not limited to metal foils such as aluminum foil and copper foil. Yet another example is a porous or microporous foam comprising thermoplastic organic polymer which foam has been compressed to such an extent that the resulting deformed material is substantially nonporous. Still another example is glass.

Base stocks which are normally porous such as for example paper, paperboard, wood, cloth, nonwoven fabric, felt, unglazed ceramic material, polymer membranes, porous foam, or microporous foam may be coated or laminated to render one or more surfaces substantially nonporous and thereby provide substrates having at least one substantially nonporous surface.

The substrate may be substantially transparent, it may be substantially opaque, or it may be of intermediate transparency. For some applications such as ink jet printed overhead slides, the substrate must be sufficiently transparent to be useful for that application. For other applications such as ink jet printed paper, transparency of the substrate is not so important.

The printing media of one embodiment Part II of the invention may be made by coating a surface of the substrate with a coating composition comprising: (a) discrete particles having a number average particle size in the range of from 1 to 500 nanometers; (b) an aqueous liquid medium; and (c) film-forming organic polymer dissolved or dispersed in the aqueous liquid medium wherein poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 20 percent by weight of the organic polymer; and thereafter substantially removing the aqueous liquid medium.



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The coating composition can be in the form of an aqueous solution in which case the aqueous liquid medium is an aqueous solvent, or the coating composition can be in the form of an aqueous dispersion in which instance the aqueous liquid  
5 medium is an aqueous dispersion liquid.

The discussions above in respect of the particles, the film-forming organic polymer, the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000, and the additional film-forming organic  
10 polymer which may optionally also be present are applicable here.

The weight ratio of the particles to organic film-forming polymer in the coating composition may vary considerably, but it is usually in the range of from 54:100 to  
15 233:100. Often the weight ratio is in the range of from 67:100 to 150:100. Preferably it is in the range of from 82:100 to 122:100.

Usually the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to  
20 3,000,000 constitutes at least 20 percent by weight of the film-forming organic polymer of the coating composition. Generally the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 51 percent by weight of the film-forming  
25 organic polymer of the coating composition. In many instances the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 60 percent by weight of the film-forming organic polymer of the coating composition. Often the poly(ethylene  
30 oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 90 percent by weight of the film-forming organic polymer of the coating

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composition. Frequently the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 95 percent by weight of the film-forming organic polymer of the coating composition. In many cases the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 99 percent by weight of the film-forming organic polymer of the coating composition. Often the poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes 100 percent by weight of the film-forming organic polymer of the coating composition.

When additional organic film-forming polymer is present, it usually constitutes from 1 to 80 percent by weight of the organic film-forming polymer of the coating composition. Generally the additional organic film-forming polymer constitutes from 1 to 49 percent by weight of the organic film-forming polymer of the coating composition. Often the additional organic film-forming polymer constitutes from 1 to 40 percent by weight of the organic film-forming polymer of the coating composition. In many cases the additional organic film-forming polymer constitutes from 1 to 10 percent by weight of the organic film-forming polymer of the coating composition. Frequently the additional organic film-forming polymer constitutes from 1 to 5 percent by weight of the organic film-forming polymer of the coating composition.

In most instances the aqueous liquid medium is water. Organic cosolvents miscible with water may optionally be present when desired. The amount of aqueous liquid medium present in the coating composition may vary widely. The minimum amount is that which will produce a coating

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composition having a viscosity low enough to apply as a coating. The maximum amount is not governed by any theory, but by practical considerations such as the cost of the liquid medium, the minimum desired thickness of the coating to be deposited, and the cost and time required to remove the aqueous liquid medium from the applied wet coating. Usually, however, the aqueous liquid medium constitutes from 75 to 98 percent by weight of the coating composition. In many cases the aqueous liquid medium constitutes from 85 to 98 percent by weight of the coating composition. Often the aqueous liquid medium constitutes from 86 to 96 percent by weight of the coating composition. Preferably aqueous liquid medium constitutes from 88 to 95 percent by weight of the composition. As a corollary, the particles having a number average particle size in the range of from 1 to 500 nanometers and the film-forming organic polymer together usually constitute from 2 to 25 percent by weight of the coating composition. Frequently such particles and the film-forming organic polymer together constitute from 2 to 15 percent by weight of the coating composition. Often such particles and the film-forming organic polymer together constitute from 4 to 14 percent by weight of the coating composition. Preferably such particles and the film-forming organic polymer together constitute from 5 to 12 percent by weight of the coating composition.

A material which may optionally be present in the coating composition is mordant. For purposes of the present specification and claims mordant is considered not to be a part of the film-forming organic polymer of the binder.

Mordants, also known as ink-fixing agents, are materials which interact, usually by reaction or absorption, with binder, dye, and/or pigment of the ink applied to the coated substrate.

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There are many available mordants which may be used. Suitable mordants include, but are not limited to, the poly(ethylenimines), the ethoxylated poly(ethylenimines), and other derivatives of poly(ethylenimine). Examples include

5 Lupasol™ SC-61B ink-fixing agent (BASF Aktiengesellschaft), Lupasol™ SC-62J mordant (BASF Aktiengesellschaft), and Lupasol™ SC-86X mordant (BASF Aktiengesellschaft), Lupasol™ PS mordant (BASF Aktiengesellschaft), Lupasol™ G-35 mordant (BASF Aktiengesellschaft), and Lupasol™ FG mordant (BASF

10 Aktiengesellschaft).

When used, the amount of mordant present in the coating composition may vary considerably. In such instances the weight ratio of the mordant to the poly(ethylene oxide) having a weight average molecular weight in the range of from

15 100,000 to 3,000,000 is usually in the range of from 0.5:100 to 30:100. Frequently the weight ratio is in the range of from 0.5:100 to 20:100. Often the weight ratio is in the range of from 1:100 to 10:100. From 2:100 to 5:100 is preferred. These ratios are on the basis of mordant dry

20 solids and poly(ethylene oxide) dry solids.

Another material which may optionally be present in the coating composition is surfactant. For purposes of the present specification and claims surfactant is considered not to be a part of the organic film-forming polymer of the

25 binder. There are many available surfactants and combinations of surfactants which may be used. Examples of suitable surfactants include, but are not limited to, Fluorad® FC-170-C surfactant (3M Company), and Triton® X-405 surfactant (Union Carbide Corporation).

30 When used, the amount of surfactant present in the coating composition may vary considerably. In such instances the weight ratio of the surfactant to the poly(ethylene oxide)

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having a weight average molecular weight in the range of from 100,000 to 3,000,000 is usually in the range of from 0.01:100 to 10:100. In many instances the weight ratio is in the range of from 0.1:100 to 10:100. Often the weight ratio is in the  
5 range of from 0.2:100 to 5:100. From 0.5:100 to 2:100 is preferred. These ratios are on the basis of surfactant dry solids and poly(ethylene oxide) dry solids.

There are many other conventional adjuvant materials which may optionally be present in the coating composition.  
10 These include such materials as lubricants, waxes, plasticizers, antioxidants, organic solvents, lakes, and pigments. The listing of such materials is by no means exhaustive. These and other ingredients may be employed in their customary amounts for their customary purposes so long  
15 as they do not seriously interfere with good coating composition formulating practice.

The pH of the coating composition may vary considerably. In most instances the pH is in the range of from 3 to 10. Often the pH is in the range of from 3 to 6.  
20 Frequently the pH is in the range of from 3 to 5.5. In many instances the pH is in the range of from 3.5 to 4.5. In other instances the pH is in the range of from 7 to 9.

The coating compositions are usually prepared by simply admixing the various ingredients. The ingredients may  
25 be mixed in any order. Although the mixing of liquid and solids is usually accomplished at room temperature, elevated temperatures are sometimes used. The maximum temperature which is usable depends upon the heat stability of the ingredients.

30 The coating compositions are generally applied to the surface of the substrate using any conventional technique known to the art. These include spraying, curtain coating,

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dipping, rod coating, blade coating, roller application, size press, printing, brushing, drawing, slot-die coating, and extrusion. The coating is then formed by removing the solvent from the applied coating composition. This may be  
5 accomplished by any conventional drying technique. Coating composition may be applied once or a multiplicity of times. When the coating composition is applied a multiplicity of times, the applied coating is usually but not necessarily dried, either partially or totally, between coating  
10 applications. Once the coating composition has been applied to the substrate, the solvent is substantially removed, usually by drying.

Optionally the above-described coatings may be overlaid with an overcoating comprising ink-receptive organic  
15 film-forming polymer. The overcoating may be formed by applying an overcoating composition comprising a liquid medium and ink-receptive organic film-forming polymer dissolved or dispersed in the liquid medium and removing the liquid medium, as for example, by drying. Preferably the liquid medium is an  
20 aqueous solvent and the ink-receptive organic film-forming polymer is water-soluble poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000, both of which have been described above in respect of earlier described embodiments of the invention. Water is  
25 an especially preferred aqueous solvent.

The relative proportions of liquid medium and organic film-forming polymer present in the overcoating composition may vary widely. The minimum proportion is that which will produce an overcoating composition having a  
30 viscosity low enough to apply as an overcoating. The maximum proportion is not governed by any theory, but by practical considerations such as the cost of the liquid medium and the

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cost and time required to remove the liquid medium from the applied wet overcoating. Usually, however, the weight ratio of liquid medium to film-forming organic polymer is from 18:1 to 50:1. Often the weight ratio is from 19:1 to 40:1.

5 Preferably weight ratio is from 19:1 to 24:1.

Optional ingredients such as those discussed above may be present in the overcoating composition when desired.

The overcoating composition may be prepared by admixing the ingredients. It may be applied and dried using  
10 any of the coating and drying techniques discussed above. When an overcoating composition is to be applied, it may be applied once or a multiplicity of times.

The gloss of the coated substrate may vary widely. Although lower glosses are acceptable for many purposes, it is  
15 preferred that the gloss be at least 20. As used herein gloss is determined according to TAPPI Standard T653 pm-90.

Part II of the invention is further described in conjunction with the following examples which are to be considered illustrative rather than limiting, and in which all  
20 parts are parts by weight and all percentages are percentages by weight unless otherwise specified.

#### EXAMPLE 11

One liter of deionized water was heated to 80°C with  
25 vigorous stirring in a large open beaker. While continuing the stirring, 71 grams of titanium isopropoxide was slowly added. A white precipitate formed immediately. Stirring at 80°C was continued for 90 minutes during which period the volume boiled down to approximately 750 milliliters. The  
30 slurry was poured into a one-liter round bottom flask. Twenty-three grams of a 10 percent by weight solution of tetramethyl ammonium hydroxide solution was added and the

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contents of the flask were refluxed overnight to form a colloidal dispersion (sol) containing 7.8 percent by weight colloidal titania.

A poly(ethylene oxide) (PEO) solution was formed by dissolving 150 grams poly(ethylene oxide) having a weight average molecular weight of about 400,000 in 2850 grams of deionized water. The mixture was stirred until all poly(ethylene oxide) was dissolved giving a composition containing 5.0 percent solids.

To 55 grams of the above PEO solution was added 28.8 grams of the above titania sol. Into this mixture was added with stirring 50 milligrams Fluorad™ FC-170-C surfactant to form a coating composition.

The coating composition was applied to commercially available glossy polyethylene-coated paper with a Meyer Rod #150 and allowed to dry under an infrared heating lamp. The dry coating was about 20 micrometers thick.

The coated paper was then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed paper showed excellent print quality.

#### EXAMPLE 12

To 120 grams of a poly(ethylene oxide) solution prepared as described in Example 11 were added 20 grams of a colloidal silica sol (Ludox® HS-40; E.I. Dupont de Nemours & Co.) containing 40 percent by weight of silica and 16 grams of a poly(ethylene-co-acrylic acid) dispersion (Adcote® 50T4983; Morton Adhesives) containing 25 percent by weight of polymer. Into this mixture was added with stirring 78 milligrams Fluorad™ FC-170-C surfactant to form a coating composition.



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The coating composition was applied to poly(ethylene terephthalate) transparencies with a Meyer Rod #150 and allowed to dry under an infrared heating lamp. The dry coating was about 20 micrometers thick and it was clear.

5           The coated transparencies were then printed on the coated side by a Hewlett-Packard 1600C ink jet printer. The ink jet printed transparencies exhibited excellent ability to maintain the edge acuity of ink patterns, excellent color fidelity, and were dry to touch as they came out of the  
10 printer. A test with a roller showed no color transfer to paper after 5 seconds. A water test showed excellent water fastness of the ink dyes in all colors. Pigmented black ink in the test patterns showed no cracking.

15                           EXAMPLE 13

To 120 grams of a poly(ethylene oxide) solution prepared as described in Example 11 were added 7.5 grams of a colloidal silica sol (Ludox® HS-40; E.I. Dupont de Nemours & Co.) containing 40 percent by weight of silica. Into this  
20 mixture was added with stirring 64 mg Fluorad™ FC-170-C surfactant to form a coating composition.

The coating composition was applied to poly(ethylene terephthalate) transparencies with a Meyer Rod #150 and allowed to dry under an infrared heating lamp. The dry  
25 coating was about 20 micrometers thick and it was clear.

The coated transparencies were then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed transparencies showed excellent print quality.

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EXAMPLE 14

Sixty-five grams of a low molecular weight, partially methylated melamine-formaldehyde resin (Resimene® AQ-7550; Monsanto Co.) containing 78% solids was added to 5 435 grams of deionized water. The mixture was stirred at room temperature until a homogeneous solution was formed. Next, concentrated hydrochloric acid was added while stirring to lower the pH to a value of 3.2. The acidified solution was then covered and placed in an oven at 85°C for 3 hours. The 10 resultant melamine-formaldehyde sol had a light blue haze resulting from Rayleigh scattering indicating a number average particle size less than 500 nanometers. The sol contained approximately 10 percent by weight of a partially crosslinked melamine-formaldehyde (MF) polymer.

15 To 55 grams of a poly(ethylene oxide) solution prepared as described in Example 11 were added 30 grams of colloidal alumina monohydroxide sol prepared as described in Example 1 of Part I and 15 grams of the above melamine-formaldehyde sol. Into this mixture was added with stirring 20 50 milligrams Fluorad™ FC-170-C surfactant to form a coating composition.

The coating composition was applied to poly(ethylene terephthalate) transparencies with a Meyer Rod #150 and allowed to dry under an infrared heating lamp. The dry 25 coating was about 20 micrometers thick and it was clear.

The coated transparencies were then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed transparencies showed excellent print quality.

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EXAMPLE 15

To 70 grams of a poly(ethylene oxide) solution prepared as described in Example 11 were added 30 grams of a melamine-formaldehyde sol prepared as described in Example 14.

5 Into this mixture was added with stirring 50 milligrams Fluorad™ FC-170-C surfactant to form a coating composition.

The coating composition was applied to poly(ethylene terephthalate) transparencies with a Meyer Rod #150 and allowed to dry under an infrared heating lamp. The dry  
10 coating was about 20 micrometers thick and it was clear.

The coated transparencies were then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed transparencies showed excellent print quality.

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EXAMPLE 16

The following initial charge and feeds shown in Table 3 were used in the preparation of aqueous secondary amine and hydroxyl functional acrylic polymer via solution  
20 polymerization technique.

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TABLE 3

	<u>Ingredients</u>	<u>Weight, grams</u>
5		
	<u>Initial Charge</u>	
	Isopropanol	130.0
	<u>Feed 1</u>	
10	Isopropanol	113.0
	n-Butyl acrylate	69.2
	Methyl methacrylate	153.0
	2-(tert-Butylamino)ethyl methacrylate	
	[CAS 3775-90-4]	73.0
15	Styrene	69.2
	VAZO <sup>1</sup> 67 Initiator <sup>1</sup>	18.2
	<u>Feed 2</u>	
	Glacial acetic acid	17.7
20	<u>Feed 3</u>	
	Deionized water	1085.0

<sup>1</sup> 2,2'-Azobis(2-methylbutanenitrile) initiator  
25 commercially available from E.I. du Pont de Nemours and Company,  
Wilmington, Delaware.

The initial charge was heated in a reactor with  
agitation to reflux temperature (80°C). Then Feed 1 was added  
30 in a continuous manner over a period of 3 hours. At the  
completion of Feed 1 addition, the reaction mixture was held at  
reflux for 3 hours. The resultant acrylic polymer solution had  
a total solids content of 61.7 percent (determined by weight  
difference of a sample before and after heating at 110°C for one  
35 hour) and number average molecular weight of 4792 as determined  
by gel permeation chromatography using polystyrene as the  
standard. Thereafter, Feed 2 was added over five minutes at  
room temperature with agitation. After the completion of the  
addition of Feed 2, Feed 3 was added over 30 minutes while the  
40 reaction mixture was heated for azeotropic distillation of

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isopropanol. When the distillation temperature reached 99°C, the distillation was continued about one more hour and then the reaction mixture was cooled to room temperature. The total distillate collected was 550.6 grams. The product, which was a cationic acrylic polymer aqueous solution, had a solids content of 32.6 percent (determined by weight difference of a sample before and after heating at 110°C for one hour), and a pH of 5.25.

To 50 grams of a poly(ethylene oxide) solution prepared as described in Example 11 were added 12.5 grams of colloidal alumina sol prepared as described in Example 1 of Part I and 4.3 grams of the above cationic acrylic polymer aqueous solution. Into this mixture was added with stirring 50 milligrams Fluorad™ FC-170-C surfactant to form a coating composition.

The coating composition was applied to poly(ethylene terephthalate) transparencies with a Meyer Rod #150 and allowed to dry under an infrared heating lamp. The dry coating was about 20 micrometers thick and it was clear.

The coated transparencies were then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed transparencies showed excellent print quality.

#### 25                    EXAMPLE 17

With stirring, 248 grams of aluminum tri-sec-butoxide [CAS 2269-22-9] was added to 2 liters of water at 75°C in a glass container. To this mixture 5.5 grams of 60 percent concentrated nitric acid was added. The reaction mixture was stirred 5 minutes on a hot plate. The glass container containing this mixture was then sealed with a lid and placed in an oven at 95°C for 3 days. During this period

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the precipitate of the mixture was peptized to a colloidal dispersion of  $\text{AlO}(\text{OH})$ . The resultant colloidal dispersion was concentrated to 1200 grams by boiling on a hot plate under stirring to produce a 5 percent by weight colloidal sol of colloidal alumina monohydroxide,  $\text{AlO}(\text{OH})$ .

To 100 grams of above prepared colloidal sol was added 4 grams of poly(ethylene oxide) having a weight average molecular weight of about 400,000. The mixture was stirred vigorously until all poly(ethylene oxide) was dissolved giving a composition containing 8.7 percent solids. Into this mixture were added with stirring 20 mg Fluorad™ FC-170-C surfactant and 0.5 gram of 5 percent Lupasol™ SC 61-B concentrated hydroxyethylated poly(ethylenimine) to form a coating composition.

The coating composition was applied to poly(ethylene terephthalate) transparencies with a Meyer Rod #150 and allowed to dry at room temperature. The dry coating was about 20  $\mu\text{m}$  thick and it was clear.

The coated transparencies were then printed on the coated side by a Hewlett-Packard 1600C ink jet printer. The ink jet printed transparencies exhibited excellent ability to maintain the edge acuity of ink patterns, excellent color fidelity, and were dry to touch as it came out of the printer.

A test with a roller showed no color transfer to paper after 5 seconds. A water test showed excellent water fastness of the ink dyes in all colors. Pigmented black ink in the test patterns showed no cracking.

#### EXAMPLE 18

The coating composition prepared in Example 12 was applied similarly onto commercially available glossy polyethylene-coated paper and onto commercially available

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gelatine-coated paper and dried. When these papers were printed on the coated side using a Hewlett-Packard 850C ink jet printer, they showed photographic quality prints with high gloss, about 90%, again with excellent color fidelity, edge acuity, and water and light fastness.

The coating composition prepared in Example 11 was applied similarly onto cloth, and aluminum foil. After the coating had dried, these coated substrates were ink jet printed with excellent results.

10

#### EXAMPLE 19

To 100 grams of colloidal alumina sol prepared in Example 12, 7 grams of poly(ethylene oxide) with a weight average molecular weight of about 200,000 was added. An additional 43 grams of water was also added to facilitate complete dissolution of the poly(ethylene oxide). The mixture was stirred until complete dissolution of the poly(ethylene oxide) took place yielding 150 grams of solution containing 12 grams of solids (8 percent solids). With stirring, one gram of Lupasol™ SC®-J 5 percent poly(ethylenimine) solution, was added to form a coating composition.

Similarly to Example 12, the coating composition was applied to transparencies and dried with a hot air blower for several minutes until the coatings were dry.

The coated transparencies were printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed transparencies showed excellent print quality.

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EXAMPLE 20

Two solutions were prepared as follows:

Solution A: A poly(ethylene oxide) (PEO) solution was formed by dissolving 150 grams poly(ethylene oxide) having a weight average molecular weight of about 400,000 in 2850 grams of water.

Solution B: 408 grams of aluminum isopropoxide was introduced to 4 liters of water at 70°C with stirring. To this mixture was added 11 grams of 60 percent concentrated nitric acid with stirring. The resulting mixture was sealed with a lid and placed in an oven at 95°C to be peptized. After 3 days, the lid was opened and the colloidal sol was allowed to evaporate to a final total weight of 800 grams and an  $\text{AlO}(\text{OH})$  concentration of 15% by weight. Various coating compositions were made by mixing these two solutions as shown in Table 4:

TABLE 4

20	Coating	Solution A,	Solution B,
	<u>Composition</u>	<u>grams</u>	<u>grams</u>
	1	200	100
	2	300	100
	3	400	100
25	4	500	100

These coating compositions were coated on poly(ethylene terephthalate) (PET) transparencies with a Meyer Rod so as to deposit films which, after drying, were approximately 20  $\mu\text{m}$  thick. All four coated transparencies were transparent with excellent ink jet printability.



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EXAMPLE 21

A 600 gram quantity of Coating Composition No. 2 of Example 20 was prepared. This was divided into six 100 gram portions. Six coating solutions were formed by introducing a mordant to each portion as shown in Table 5:

TABLE 5

10	Coating Solution Number	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
15	Coating Composition No. 2, grams	100	100	100	100	100	100
20	5% Aqueous Lupasol™ SC 61-B Mordant, grams	1	5	0	0	0	0
25	5% Aqueous Lupasol™ SC 62-J Mordant, grams	0	0	1	5	0	0
30	5% Aqueous Lupasol™ SC 86-X Mordant, grams	0	0	0	0	1	5

These solutions were each coated on a separate poly(ethylene terephthalate) transparency approximately 20-25µm thick. After drying, the coated transparencies were printed on the coated side by a Hewlett-Packard 1600C ink jet printer. The quality of the print was excellent on all of them and all showed excellent water fastness of all colors.

EXAMPLE 22

With stirring 22.35 kg. of aluminum tri-secondary butoxide was charged with stirring into a reactor containing 75 kg of water at about 78°C. Four hundred twenty grams of

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70% nitric acid was diluted in 1110 grams of water and added into the same reactor immediately after the charging of aluminum tri-secondary butoxide. The system was closed when the reactor was heated to about 120°C gaining pressure to about 276 kilopascals, gauge. The reactor was held at this temperature for 5 hours then cooled to 70°C and opened. Then the reactor was heated to boil off the alcohol and water-alcohol azeotrope of the hydrolysis reaction until the concentration of the sol reached about 10 weight percent AlO(OH), about 54 kg. total, having a pH of 3.8-4.0 and a turbidity of 112.

Into 90 grams of this colloidal alumina sol, 11 grams of poly(ethylene oxide) having a weight average molecular weight of about 400,000 and 150 grams of water were added and stirred until the poly(ethylene oxide) was completely dissolved. Into this sufficient nitric acid was added to lower the pH to within a range of 3.5 to 4.0. Then 12.5 grams of 5% Lupasol™ SC 61-B mordant was added followed by the addition of 0.075 gram of Fluorad™ FC-170-C surfactant.

After mixing, the solution was coated on poly(ethylene terephthalate) transparencies using a Meyer Rod #150. The coating was heat dried. No haze was observed.

The coated transparencies were printed on the coated side by a Hewlett-Packard 1600C ink jet printer to produce printed transparencies having excellent print quality, edge acuity, and color fidelity. Ink drying time was less than 5 seconds. The printed transparencies were free from observed scratches and ink cracking.

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## CLAIMS:

1. A printing medium comprising:
  - (a) a substrate having at least one surface, and
  - 5 (b) a substantially nonporous coating on said surface wherein said coating comprises transparent, colorless alumina monohydroxide and water-soluble organic polymer, and wherein said water-soluble organic polymer comprises
  - 10 water-soluble cellulosic organic polymer and water-soluble noncellulosic organic polymer.
2. The printing medium of claim 1 wherein said surface of said substrate is substantially nonporous.
- 15 3. The printing medium of claim 1 wherein said transparent, colorless alumina monohydroxide constitutes from 10 to 87 percent by weight of the coating.
- 20 4. The printing medium of claim 1 wherein said transparent, colorless alumina monohydroxide is transparent, colorless pseudo-boehmite.
- 25 5. The printing medium of claim 1 wherein said water-soluble organic polymer constitutes from 13 to 90 percent by weight of said coating.
6. The printing medium of claim 1 wherein said substrate is coated paper.
- 30 7. The printing medium of claim 1 wherein said coating is substantially transparent.

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8. The printing medium of claim 7 wherein said substrate is substantially transparent.

5 9. The printing medium of claim 8 wherein said substantially transparent substrate is a sheet or film of substantially transparent organic polymer.

10 10. The printing medium of claim 9 wherein said substantially transparent organic polymer of said substantially transparent substrate is poly(ethylene terephthalate) or cellulose acetate.

15 11. The printing medium of claim 1 wherein said water-soluble cellulosic organic polymer constitutes from 5 to 95 percent by weight of said water-soluble organic polymer and said water-soluble noncellulosic organic polymer constitutes from 5 to 95 percent by weight of said water-soluble organic polymer.

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12. The printing medium of claim 1 wherein:

(a) said water-soluble cellulosic organic polymer comprises water-soluble hydroxypropylcellulose, and

25 (b) said water-soluble noncellulosic organic polymer comprises water-soluble poly(vinyl alcohol).

30 13. The printing medium of claim 12 wherein the weight average molecular weight of said water-soluble hydroxypropylcellulose is in the range of from 200,000 to 400,000.

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14. The printing medium of claim 12 wherein said water-soluble poly(vinyl alcohol) is fully hydrolyzed water-soluble poly(vinyl alcohol).

5

15. The printing medium of claim 1 wherein said coating is overlaid with an overcoating comprising ink-receptive organic polymer.

10 16. The printing medium of claim 15 wherein said ink-receptive organic polymer comprises water-soluble hydroxypropylcellulose.

15 17. A printing medium comprising:  
(a) a substrate having at least one surface, and  
(b) a substantially nonporous coating on said surface wherein said coating comprises transparent, colorless alumina monohydroxide and partially or completely insolubilized  
20 water-soluble organic polymer.

18. The printing medium of claim 17 wherein said surface of said substrate is substantially nonporous.

25 19. The printing medium of claim 17 wherein said coating is overlaid with an overcoating comprising ink-receptive organic polymer.

30 20. The printing medium of claim 19 wherein said ink-receptive organic polymer comprises water-soluble hydroxypropylcellulose.

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21. A coating composition comprising:

- (a) transparent, colorless alumina monohydroxide;
- (b) aqueous solvent; and
- (c) water-soluble organic polymer dissolved in

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said aqueous solvent;

wherein said water-soluble organic polymer comprises  
water-soluble cellulosic organic polymer and water-soluble  
noncellulosic organic polymer.

10

22. The coating composition of claim 21 wherein:

- (a) the weight ratio of said alumina monohydroxide  
to said water-soluble organic polymer is in  
the range of from 11:100 to 670:100, and
- (b) said water-soluble cellulosic organic polymer

15

constitutes from 5 to 95 percent by weight of  
said water-soluble organic polymer and said  
water-soluble noncellulosic organic polymer  
constitutes from 5 to 95 percent by weight of  
said water-soluble organic polymer.

20

23. The coating composition of claim 21 wherein  
said aqueous solvent constitutes from 80 to 98 percent by  
weight of said coating composition.

25

24. The coating composition of claim 21 wherein:

- (a) said water-soluble cellulosic organic polymer  
comprises water-soluble  
hydroxypropylcellulose, and
- (b) said water-soluble noncellulosic organic

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polymer comprises water-soluble poly(vinyl  
alcohol).

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25. The coating composition of claim 24 wherein the weight average molecular weight of said water-soluble hydroxypropylcellulose is in the range of from 200,000 to 400,000.

5

26. The coating composition of claim 24 wherein said water-soluble poly(vinyl alcohol) is fully hydrolyzed water-soluble poly(vinyl alcohol).

10

27. The coating composition of claim 21 which further comprises insolubilizer.

28. The coating composition of claim 27 wherein the weight ratio of said insolubilizer to said water-soluble noncellulosic organic polymer is in the range of from 0.05:100 to 25:100.

29. A printing medium comprising:

(a) a substrate having at least one surface; and

20 (b) a coating on said surface wherein said coating comprises:

(1) a binder comprising organic polymer, wherein poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 20 percent by weight of said organic polymer; and

25 (2) discrete particles dispersed in said binder, which particles have a number average particle size in the range of

30 from 1 to 500 nanometers.

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30. The printing medium of claim 29 wherein the number average particle size of said discrete particles is in the range of from 1 to 100 nanometers.

5 31. The printing medium of claim 29 wherein the number average particle size of said discrete particles is in the range of from 1 to 50 nanometers.

10 32. The printing medium of claim 29 wherein the number average particle size of said discrete particles is in the range of from 1 to 20 nanometers.

15 33. The printing medium of claim 29 wherein said discrete particles constitute from 20 to 70 percent by weight of said coating.

20 34. The printing medium of claim 29 wherein said discrete particles are discrete inorganic particles, discrete crosslinked organic particles, or a mixture thereof.

35. The printing medium of claim 29 wherein said discrete particles are discrete particles of crosslinked organic polymer.

25 36. The printing medium of claim 29 wherein said discrete particles are discrete particles of metal oxide.

30 37. The printing medium of claim 36 wherein said metal oxide comprises at least one member selected from the group comprising alumina, silica, and titania.



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38. The printing medium of claim 36 wherein said metal oxide comprises alumina.

39. The printing medium of claim 38 wherein said alumina is alumina monohydroxide.

40. The printing medium of claim 39 wherein said alumina monohydroxide is pseudo-boehmite.

41. The printing medium of claim 39 wherein said alumina monohydroxide is transparent and colorless.

42. The printing medium of claim 36 wherein said metal oxide comprises colloidal silica.

43. The printing medium of claim 36 wherein said metal oxide comprises colloidal titania.

44. The printing medium of claim 29 wherein said organic polymer constitutes from 30 to 80 percent by weight of said coating.

45. The printing medium of claim 29 wherein said organic polymer comprises additional organic polymer other than said poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000.

46. The printing medium of claim 45 wherein said additional organic polymer is water-soluble poly(ethylene oxide) having a weight average molecular weight below 100,000, water-soluble poly(ethylene oxide) having a weight average molecular weight above 3,000,000, water-soluble cellulosic

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organic polymer, water-soluble noncellulosic organic polymer,  
and water dispersible polymer

47. The printing medium of claim 45 wherein said  
5 additional organic polymer is water-soluble anionic  
poly(meth)acrylate or water-soluble cationic  
poly(meth)acrylate.

48. The printing medium of claim 45 wherein:  
10 (a) said water-soluble poly(ethylene oxide) having  
a weight average molecular weight in the range  
of from 100,000 to 3,000,000 constitutes at  
least 60 percent by weight of said organic  
polymer of said binder; and  
15 (b) said additional organic polymer constitutes  
from 1 to 40 percent by weight of said organic  
polymer of said binder.

49. The printing medium of claim 29 wherein:  
20 said poly(ethylene oxide) having a weight average molecular  
weight in the range of from 100,000 to 3,000,000 constitutes  
at least 99 percent by weight of said organic polymer of said  
binder.

25 50. The printing medium of claim 29 wherein said  
substrate is coated paper.

51. The printing medium of claim 29 wherein said  
coating is substantially transparent.

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52. The printing medium of claim 29 wherein said coating is overlaid with an overcoating comprising ink-receptive organic polymer.

5 53. The printing medium of claim 52 wherein said ink-receptive organic polymer comprises water-soluble poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000.

10 54. The printing medium of claim 29 wherein the thickness of said coating is in the range of from 5 to 40 micrometers.

55. A coating composition comprising:  
15 (a) discrete particles having a number average particle size in the range of from 1 to 500 nanometers;  
(b) an aqueous liquid medium; and  
(c) film-forming organic polymer dissolved or  
20 dispersed in said aqueous liquid medium wherein water-soluble poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 20 percent by weight of  
25 said organic polymer.

56. The coating composition of claim 55 wherein the number average particle size of said discrete particles is in the range of from 1 to 100 nanometers.

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57. The coating composition of claim 55 wherein the number average particle size of said discrete particles is in the range of from 1 to 50 nanometers.

5 58. The coating composition of claim 55 wherein the number average particle size of said discrete particles is in the range of from 1 to 20 nanometers.

59. The printing medium of claim 55 wherein said  
10 discrete particles constitute from 20 to 70 percent by weight of said coating.

60. The printing medium of claim 55 wherein said discrete particles are discrete inorganic particles, discrete  
15 crosslinked organic particles, or a mixture thereof.

61. The printing medium of claim 55 wherein said discrete particles are discrete particles of crosslinked organic polymer.  
20

62. The coating composition of claim 55 wherein said discrete particles are discrete particles of metal oxide.

63. The coating composition of claim 62 wherein  
25 said metal oxide comprises at least one member selected from the group comprising alumina, silica, and titania.

64. The coating composition of claim 62 wherein said metal oxide comprises alumina.  
30

65. The coating composition of claim 64 wherein said alumina is alumina monohydroxide.

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66. The coating composition of claim 65 wherein said alumina monohydroxide is pseudo-boehmite.

5           67. The coating composition of claim 65 wherein said alumina monohydroxide is transparent and colorless.

68. The coating composition of claim 62 wherein said metal oxide comprises colloidal silica.

10

69. The coating composition of claim 62 wherein said metal oxide comprises colloidal titania.

70. The coating composition of claim 55 wherein  
15 said organic polymer constitutes from 30 to 80 percent by weight of said coating.

71. The coating composition of claim 55 wherein said organic polymer comprises additional organic polymer  
20 other than said poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000.

72. The printing medium of claim 71 wherein said additional organic polymer is water-soluble poly(ethylene  
25 oxide) having a weight average molecular weight below 100,000, water-soluble poly(ethylene oxide) having a weight average molecular weight above 3,000,000, water-soluble cellulosic organic polymer, water-soluble noncellulosic organic polymer, water dispersible polymer, or a mixture of two or more  
30 thereof.

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73. The printing medium of claim 71 wherein said additional organic polymer is water-soluble anionic polyacrylate or water-soluble cationic polyacrylate.

- 5                   74. The coating composition of claim 71 wherein:
- (a) said water-soluble poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 60 percent by weight of said organic
- 10                   polymer of said binder; and
- (b) said additional organic polymer constitutes from 1 to 40 percent by weight of said organic polymer of said binder.

- 15                   75. The coating composition of claim 55 wherein said poly(ethylene oxide) having a weight average molecular weight in the range of from 100,000 to 3,000,000 constitutes at least 99 percent by weight of said organic polymer of said binder.

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